

Silver Halides as the Basis for Novel Photonic Materials

M. R. V. Sahyun, Matthew Goertz, Erin D. Moritz, Amy Rassbach, and Scott N. Thorgaard

*Chemistry Department, University of Wisconsin—Eau Claire
Eau Claire, WI (USA)*

Nanocrystalline silver halides are well-known and easily and reproducibly prepared¹. In photographic technology they are the bases for, e.g., Lippman color photography and photosensitivity of photothermographic media. Beginning with observations several years ago of optical bistability in nano-AgBr dispersions², we have continued to explore possible applications of these materials in non-linear optics. It is the purpose of this presentation to review these investigations.

Nano-AgBr has been found by Hyper-Rayleigh Scattering Spectroscopy (HRS) to exhibit substantial second-order hyperpolarizability, despite its centrosymmetric bulk crystal structure. We therefore identified this response with surface states; experimental and theoretical data suggest surface silver ad-ions³.

Both optical switching and second-order scattering can be enhanced by sensitizing dye adsorption. In the former case² the mechanism may be analogous to spectral sensitization of photographic response, but in the latter we infer surface enhancement of second harmonic scattering (SESHS), with the dye molecule itself as hyperpolarizable chromophore³.

Nano-AgBr dispersions can be converted to nanosilver, in a process analogous to photographic development⁴. Well-characterized, reproducible silver nanosols result. Like nano-AgBr, nanosilver exhibits a large, useful second-order hyperpolarizability, typical of nanometals⁵. The particles have a reactive surface (oxide or halide monolayer) which gives rise to a rich surface chemistry, e.g., formation of a hexagonally close-packed AgI monolayer on reaction with iodide. This conversion, which finds precedent in the literature⁶ bleaches the plasmon resonance band of the nanosilver.

Surface reactivity also enables chemisorption of a reactive merocyanine dye⁴. Evidence of J-aggregation is obtained; absence of second-order response from the dye

aggregates suggests head-to-tail geometry. Higher levels of dye exhibit a modicum of SESHs, however.

References

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Biography

M. R. V. (Mel) Sahyun received his Ph.D. in physical chemistry from UCLA, where he was an NSF Pre-doctoral Fellow. He was an NIH Research Fellow at the California Institute of Technology after a period of service in the US Public Health Service in Bethesda, MD, where he was involved in their environmental science program. His principal career position was at the Corporate Research Laboratories of 3M, Maplewood, MN, where he specialized in silver halide and electrophotographic imaging processes, along with molecular photochemistry. Subsequently he has been Adjunct Professor in the Chemistry Department of the University of Wisconsin—Eau Claire.

Dr. Sahyun is a Fellow and Senior Member of IS&T, has received the Society's Journal Award (1996), served as Vice-President, and has been the Editor of the *Journal of Imaging Science and Technology* since 1996.